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(54) PHOTOCATALYST BODY AND METHOD OF PRODUCTION THEREOF

(57) The invention relates to a photocatalytic body having a good photocatalytic function characterized by using an amorphous titanium peroxide sol, and a method for making the same. A photocatalyst such as titanium oxide in the form of powder or a sol and an amorphous titanium peroxide sol are mixed in different mixing rations depending on the purpose in use and the resultant mixture is coated onto a substrate such as an organic polymer resin, dried・solidifed and/or baked to support and fixed the photocatalyst on the substrate to make a photocatalytic body. Alternatively, a first layer consisting of an amorphous titanium peroxide sol on a substrate, and a second layer made of a photocatalyst is formed on the first layer to make a photocatalytic body.

According to the invention, the photocatalyst can be supported and fixed on the substrate without lowering the photocatalytic function of the photocatalyst to obtain a photocatalytic body which is usable over a long time.

The amorphous titanium peroxide sol used in the practice of the invention may be prepared, for example, by the following manner. An alkali hydroxide such as aqueous ammonia or sodium hydroxide is added to an aqueous solution of a titanium salt such as titanium tetrachloride, $TiCl_4$. The resultant light bluish white, amorphous titanium hydroxide, $Ti(OH)_4$, may be called orthotitanic acid, H_4TiO_4. This titanium hydroxide is washed and separated, after which it is treated with an aqueous hydrogen peroxide solution to obtain an amorphous titanium peroxide solution useful in the present invention. The amorphous titanium peroxide sol has a pH of 6.0 ~ 7.0 and a particle size of 8 ~ 20 nm, with its appearance being in the form of a yellow transparent liquid. The sol is stable when stored at normal temperatures over a long time. The sol concentration is usually adjusted to a level of 1.40 ~ 1.60%. If necessary, the concentration may be optionally controlled. If the sol is used at low concentrations, it is used by dilution such as with distilled water.

The amorphous titanium peroxide sol remains as amorphous and is not crystallized in the form of anatase titanium oxide at normal temperatures. The sol has good adherence, a good film-forming property and is able to form a uniform flat thin film, and a dried film has such a property of being insoluble in water.

It will be noted that when the amorphous titanium peroxide sol is heated to 100°C or above, it is converted to anatase titanium oxide sol. The amorphous titanium peroxide sol, which has been dried and fixed on a substrate after coating, is converted to anatase titanium oxide when heated to 250°C or above.

The photocatalysts usable in the present invention include TiO_2, ZnO, $SrTiO_3$, CdS, CdO, CaP, InP, In_2O_3, CaAs, $BaTiO_3$, K_2NbO_3, Fe_2O_3, Ta_2O_5, WO_3, SaO_2, Bi_2O_3, NiO, Cu_2O, SiC, SiO_2, MoS_2, MoS_3, InPb, RuO_2, CeO_2 and the like. Of these, titanium oxide is preferred. Titanium oxide may be used in the form of particles or powder, or in the form of a sol.

Titanium oxide in the form of a sol, i.e. a titanium oxide sol, can be prepared by heating an amorphous titanium peroxide sol at a temperature of 100°C or above. The properties of the titanium oxide sol, more or less, change depending on the heating temperature and the heating time. For instance, an anatase titanium oxide sol which is formed by treatment at 100°C for 6 hours has a pH of 7.5 ~ 9.5 and a particle size of 8 ~ 20 nm, with its appearance being in the form of a yellow suspension.

The titanium oxide sol is stable when stored at normal temperatures over a long time and may form a precipitate on mixing with an acid or a metal aqueous solution. Moreover, the sol may be impeded in its photocatalytic activity or an acid resistance when Na ions coexists. The sol concentration is usually adjusted to a level of 2.70 ~ 2.90% and may be employed after adjustment of the concentration, if necessary.

A titanium oxide sol is preferably used as a photocatalyst. Commercially available "ST-01" (ISHIHARA SANGYOU KAISHA Ltd) or "ST-31" (ISHIHARA SANGYOU KAISHA Ltd) may also be usable.

In the practice of the invention, the substrate used may be made of inorganic materials such as ceramics, glass and the like, organic materials such as plastics, rubber, wood, paper and the like, and metals such as aluminium, steels and the like. Of these, applications to organic polymer resin materials, such as acrylonitrile resin, vinyl chloride resin, polycarbonate resins, methyl methacrylate resin (acrylic resins), polyester resins, polyurethane resins and the like, show good effects. The substrate is not critical with respect to the size or shape and may be in the form of a honeycomb, fibers, a filter sheet, a bead, a foamed body or combinations thereof. If a substrate which allows transmission of UV light is used, a photocatalytic body may be applied to the inner surface of the substrate. The body may also be applicable to coated articles.

In the present invention, binders which are incapable of being decomposed with a photocatalyst mean those binders incapable of being decomposed with photocatalysts and composed of inorganic binders such as water glass, colloidal silica, cement and the like, and organic binders such as fluoropolymers, silicone polymers and the like, as disclosed in the aforementioned JP-A7-171408.

The composition used to make a photocatalytic body may be prepared according to several methods.

One of such methods includes the use of a uniform suspension of titanium oxide powder in an amorphous titanium peroxide sol. For the uniform suspension, it is advantageous to employ ultrasonic wave after mechanical agitation.

Next, the titanium oxide sol and the amorphous titanium oxide sol are mixed to obtain a mixed sol. The mixing ratio is determined depending on the portion of a product to which a photocatalytic body is applied and the use conditions of an instrument using the body. For the mixing, consideration should be taken to the adherence to a substrate, film-forming properties, corrosion resistance and decorativeness of the photocatalytic body made by use of the mixed sol. The mixing ratio can be properly determined depending on the types of articles to be applied which are broadly classified into the following three groups.

(1) Those articles which one contacts or is highly likely to contact and which need decorativeness from the visual standpoint, e.g. interior tiles, sanitary wares, various types of unit articles, tablewares, exterior materials in buildings, interior automotive trims and the like.
(2) Those articles which one does not contact but requires visual decorativeness, e.g. exterior panels for light fittings, underground passage, tunnel, materials for engineering works, and electrical equipments.

type light-emitting ceramic. Thus, the photocatalytic function is continued if the UV irradiation against the photocatalytic body is interrupted. Moreover, the particles of the spontaneous light-emitting ceramic or the light storage-type light-emitting ceramic usually emanates green, blue or orange-colored visible light, which may be utilized for decoration or directional sign in the dark.

When the photocatalytic semiconductor is controlled in its composition (by addition of inorganic pigments or metals), or is controlled in thermal treatment during the course of the preparation, it can be possible to change a wavelength (absorption band) of UV light necessary for showing the catalytic function, i.e. an excitation wavelength. For instance, if CrO_3 is added to TiO_2 in small amounts, the absorption band is shifted toward a side of a longer wavelength. This permits the photocatalytic body to be in coincidence with the emission spectral characteristics of a spontaneous UV radiating material or a light storage-type UV radiating material. Proper choice of a photocatalytic semiconductor in coincidence with a wavelength of UV light to be applied thereto becomes possible.

In contrast, the emission spectral characteristics of a spontaneous UV radiating material or a light storage-type UV radiating material may be brought into coincidence with the excitation wavelength of a photocatalytic semiconductor. For instance, the excitation wavelength of titanium oxide is in the range of 180 nm ~ 400 nm. Light storage-type UV radiating materials responsible for the wavelength have never been commercially available.

Light storage ceramics which are commercially available and permit afterglow over a long time include "Luminova" series of NEMOTO & CO., LTD, with some of the series having an afterglow time exceeding 1000 minutes. The light storage ceramics of the long-time afterglow are prepared by adding alumina to a starting main material such as strontium carbonate or calcium carbonate, further adding europium or dysprosium as an activator, and then adding an element such as of lanthanum, cerium, praseodymium, samarium, cadmium, terbium, holmium, erbium, thulium, ytterbium, ruthenium, manganese, tin and bismuth and boric acid as a flux, followed by thermal treatment at 1300°C. The product obtained by this mixing procedure is a blue light emitter having a peak of the shortest wavelength of 440 nm.

In order to shift the emission wavelength to 400 nm or below which corresponds to the excitation wavelength of titanium oxide, additive metal elements may be added for causing the absorption wavelength of the "Luminova" with a peak at 360 nm and the emission wavelength with a peak at 440 nm to come close to each other. Alternatively, if an emission wavelength of 440 nm or below does not generate on the emission of blue light at approximately 450 nm which is a phosphorescent wavelength characteristic inherent to minerals such as strontium, potassim and borax, a mineral element, which does not emanate any phosphorescent color, is shorter in wavelength than strontium, and has an emission wavelength of 400 nm or below without development of any color, may be purified and formulated to develop a light storage-type UV radiating material.

The photocatalytic semiconductor may be preliminarily supported on only the surfaces of unit particles, or may be supported on the entire surface of a molding after mixing of unit particles with the particles of a spontaneous light emitting ceramic or a light storage ceramic or the mixed particles and molding the mixture. In the former case, little photocatalytic semiconductor is deposited on the surfaces of the particles of a spontaneous light emitting ceramic or a light storage ceramic or the mixed particles, so that the quantity of UV light radiated from these particles becomes greater. With the particles of the light storage-type ceramic particles, UV light from outside can be efficiently absorbed.

The photocatalytic body may be admixed with photocatalytic function-assisting additive metals (Pt, Ag, Rh, RuO, Nb, Cu, Sn, NiO and the like) during the course of its preparation. These additives are well known as facilitating the photocatalytic reaction.

BEST MODE FOR CARRYING OUT THE INVENTION

The invention is more particularly described by way of References and Examples, which should not be construed as limiting the scope of the invention hereto.

Reference 1 (Preparation of an amorphous titanium peroxide sol)

A 1:70 dilution of a 50% solution of titanium tetrachloride, $TiCl_4$, (SUMITOMO SITX CO.) with distilled water and a 1:10 dilution of a 25% solution of ammonium hydroxide, NH_4OH, (TAKASUGI PURECHEMICAL INDUSTRY Ltd) with distilled water are mixed at a ratio by volume of 7:1 for neutralization reaction. After completion of the neutralization reaction, the pH is adjusted to 6.5 ~ 6.8 and the mixture was allowed to stand for a while, followed by discarding the supernatant liquid. Distilled water is added to the resultant $Ti(OH)_4$ in an amount of about 4 times the gel, followed by sufficient agitation and allowing to stand. While checking with silver nitrate, washing is repeated until no chlorine ion was detected in the supernatant liquid. Finally, the supernatant liquid is discarded to leave a gel alone. In some case, the gel may be subjected to centrifugal dehydration. 210 ml of an aqueous 35% hydrogen peroxide solution is divided into halves and added to 3600 ml of light yellowish white $Ti(OH)_4$ in every 30 minutes, followed by agitation at about 5°C overnight to obtain about 2500 ml of a yellow transparent amorphous titanium peroxide sol.

If the generation of heat is not suppressed in the

agitating for about 15 minutes and further agitating by means of ultrasonic waves in order not to leave flocs. Dipping was effected at a rate of 0.3 ~ 0.5 cm/second, followed by drying overnight at 30°C. This was baked at 400°C for 30 minutes to make a photocatalytic body.

The photocatalyst layer was firmly bonded to the tile surface over a long time.

On the other hand, when the tile was coated with a dispersion of the titanium oxide powder in distilled water, good bonding was not attained.

Example 4

A float glass which had been degreased and treated with a surface active agent was coated on the surface thereof with a glass beads suspension by means of a spray gun several times. After drying at 40°C, the coating was baked at 700°C for 30 minutes. The float glass on which the glass beads was fixed was further coated with a photocatalyst composition used in Example 3, dried and baked at 400°C for 30 minutes to obtain a photocatalytic body. This photocatalytic body was strongly bonded to the glass beads fixed on the float glass over a long time.

Example 5

A light storage-type UV radiating material "KEPRUS" (commercial name of Next • I CO., LTD) was mixed with an amorphous titanium peroxide sol in an amount of 25 wt% based on the titanium peroxide in the sol, agitated, sprayed over a KERAMIT decorative sheet used as a substrate, dried at normal temperature, baked at 400°C for 30 minutes, and cooled. Thereafter, a titanium oxide sol whose excitation wavelength was adjusted to an emission wavelength of the radiating material was sprayed in a thickness of 1 μm, dried and baked at 40°C for 30 minutes. The resultant photocatalytic body had the photocatalytic action continued by means of the UV light emanated from the UV radiating material when irradiation of the UV light against the body was interrupted.

INDUSTRIAL APPLICABILITY

According to the invention, a photocatalyst can be supported and fixed on a substrate without lowering the photocatalytic function of the photocatalyst thereby providing a photocatalytic body which is usable over a long time. The photocatalytic body of the invention can be used as interior and exterior members for buildings such as interior and exterior tiles, sanitary wares, air conditioners, bathtubs and the like, exterior panels of various types of electric equipments such as lightning fittings, interior automotive members, inner walls of underground passage and tunnel, water-purifier tanks and the like.

Claims

1. A method for making a photocatalytic body wherein a photocatalyst is supported and fixed on a substrate, characterized in that an amorphous titanium peroxide sol is used as the photocatalyst.

2. A method for making a photocatalytic body as claimed in Claim 1, characterized in that particles of titanium oxide or powder of titanium oxide is used as the photocatalyst.

3. A method for making a photocatalytic body as claimed in Claim 1, characterized in that a titanium oxide sol is used as the photocatalyst.

4. A method for making a photocatalytic body as claimed in Claim 3, characterized by using a mixed sol wherein the titanium oxide sol is mixed in an amount of 30 wt% or below based on the total of the titanium oxide sol and the amorphous titanium peroxide sol.

5. A method for making a photocatalytic body as claimed in Claim 3, characterized by using a mixed sol wherein the titanium oxide sol is mixed in an amount of 20 ~ 80 wt% based on the total of the titanium oxide sol and the amorphous titanium peroxide sol.

6. A method for making a photocatalytic body as claimed in Claim 3, characterized by using a mixed sol wherein the titanium oxide sol is mixed in an amount of 70 wt% or above based on the total of the titanium oxide sol and the amorphous titanium peroxide sol.

7. A method for making a photocatalytic body characterized by comprising, on a substrate, a first layer made of a binder incapable of decomposition by the action of a photocatalyst, and a second layer formed on said first layer and made of a photocatalyst and an amorphous titanium peroxide sol.

8. A method for making a photocatalytic body characterized by comprising, on a substrate, a first layer made of an amorphous titanium peroxide sol and having no photocatalytic function, and a second layer formed on said first layer and made of a photocatalyst and an amorphous titanium peroxide sol.

9. A method for making a photocatalytic body as claimed in Claim 7 or 8, characterized in that said second layer is formed of particles of titanium oxide or powder of titanium oxide used as a photocatalyst and an amorphous titanium peroxide sol.

10. A method for making a photocatalytic body as

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/00767

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 B01J21/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^6 B01J21/06, C01G23/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1996
Kokai Jitsuyo Shinan Koho 1971 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 62-283817, A (Catalysts & Chemical Industries Co., Ltd.), December 9, 1987 (09. 12. 87), Claim 1 (Family: none)	1 - 19
PA	JP, 8-257399, A (Chubu Electric Power Co., Inc.), October 8, 1996 (08. 10. 96), Claim 1; page 3, column 4, line 14 (Family: none)	1 - 19
PA	JP, 8-229549, A (Nippon Shokubai Co., Ltd.), September 10, 1996 (10. 09. 96), Page 3, column 4, line 42 to page 4, column 5, line 12; page 4, column 5, lines 42 to 48, column 6, lines 19 to 25 (Family: none)	1 - 19
EA	JP, 9-71418, A (Saga Prefectural Government) March 18, 1997 (18. 03. 97), Claims 1 to 3; page 2, column 2, lines 30 to 48; page 3, column 4, lines 6 to 9 (Family: none)	1 - 19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
June 5, 1997 (05. 06. 97)	June 17, 1997 (17. 06. 97)
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